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THE APPLICATION OF DIFFERENT COMPONENT SCHEMES TO PREDICT WOOD PYROLYSIS AND FIRE BEHAVIOUR

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ABSTRACT
An analytical method and a genetic algorithm searching method are used to estimate the kinetic properties of wood based on the assumptions of two different multiple-component schemes. The pyrolysis model in Fire Dynamics Simulator is used to model material-scale and bench-scale experiments using the kinetic properties derived from the two methods. It is found that the use of the kinetic properties from the different methods and the different component assumptions cause slight differences in the prediction of pyrolysis behaviour for the material-scale experiments, however, no significant differences are found in the prediction of heat release rate for bench-scale experiments.

Keywords: TGA, genetic algorithm, component schemes, FDS simulations, wood pyrolysis

1. INTRODUCTION

The decomposition kinetics of wood determines the release rate and the composition of flammable pyrolysate, which thereby affects the likelihood of ignition and subsequent flame spread rate. In order to describe the complex decomposition of wood, a multiple-component scheme [1] has been widely adopted to simplify the decomposition into several parallel reactions. Li et al. [1] suggested that the Kissinger method [2] can easily identify the pre-exponential factor and activation energy for each reaction in a multiple-component scheme but the reaction order needs to be determined by other approaches (such as a first reaction order). However, the overall matching condition to thermogravimetric (TG) curves by applying a forced reaction order is not as good as using complex searching methods such as a genetic algorithm (GA) which can find the effective solutions of reaction order [1]. In addition, the suitability of applying the assumption of multiple components for wood to predict the pyrolysis and burning behaviour for real fires is an uncertain factor.

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In this study, the Kissinger method, combined with a first reaction order model, is applied to estimate the kinetic properties of wood based on two different multiple-component schemes. A GA searching method is also adopted to find the kinetic properties. Fire Dynamics Simulator, version 6.1.0 (FDS6) [3] is employed to model both material-scale and bench-scale experiments to further evaluate the accuracy and suitability of the estimated properties in predicting the pyrolysis and burning behaviour of real fires.

2. METHODOLOGY

2.1 Wood pyrolysis model

The multiple-component decomposition scheme in this study assumes wood is composed of several major components and each component independently undergoes a reaction over a distinct temperature range, i.e. a parallel reaction scheme. The reaction rate for the i^{th} component is specified by the Arrhenius law:

$$r_i = A_i \exp(-E_i / RT)(Y_i)^{n_i} \tag{1}$$

where Y_i is the normalised mass fraction of the i^{th} component; and A_i, E_i and n_i are the pre-exponential factor (s^{-1}), activation energy (kJ/mol) and reaction order respectively, often referred to as the kinetic triplet. The total pyrolysis rate of wood can be written as Equation 2 [1], where $f_i = m_{i0}/m_0$ is the initial mass fraction of each component.

$$r = d(m/m_0)/dT = \sum_{i=1}^{M} f_i r_i \tag{2}$$

2.2 Methods to derive kinetic properties

In order to determine the decomposition rate for the pyrolysis process, the kinetic triplet for each reaction needs to be defined. A common approach is to use curves from TG experiments which record the changes in mass during decomposition. In this study, two inverse derivation methods are applied to the TG curves: one is an analytical method and the other uses a GA method.

For the analytical method proposed by Kissinger [2], the reaction order n cannot be determined, and for simplicity, all reaction orders are assumed to be one. The Kissinger method uses the value of $T_{i,p}$ for the maximum reaction rate of the i^{th} reaction occurring at different heating rates and to further develop the linear relationship between $ln(\beta/T_{i,p}^2)$ and $1/T_{i,p}$ as:

$$\ln(\beta / T_{i,p}^2) = -E_i / RT_{i,p} + \ln(A_i R / E_i) \tag{3}$$

where E_i and A_i can be identified through the slope and line intercept.

A GA method is a heuristic searching method based on Darwinian survival-of-the fittest theory. GA-based searching methods have been widely used in the decomposition model to search for values for the kinetic and stoichiometric parameters [1, 4]. GA is able to produce a large search space in a complex landscape to avoid being trapped in numerous local maxima and minima and TG experiments conducted under different heating rates can be optimised simultaneously by simply increasing the number of experimental data points.

2.3 Experiments

Two types of experiments are carried out in this work: material-scale (TG) and bench-scale (cone calorimeter) experiments. The wood samples adopted in this study are the same materials used in a large-scale fire testing programme [5]. TG experimental curves for the wood decomposition are obtained through a SDT Q600 thermal analyzer. A sample of about 10 mg of wood is placed in an aluminium crucible (5 mm in diameter) for each experiment. Three sets of experiments are conducted in a nitrogen environment heating up from ambient temperature to 800 K at a constant rate of 5, 20 and 60 K/min respectively. Each experiment is repeated three times. The cone calorimeter experiments are performed using samples in a board-like shape with an approximate exposed area of 100 mm × 100 mm. The unexposed surfaces of the samples are placed on a mineral-based insulation. Two incident heat fluxes of 35 kW/m^2 and 50 kW/m^2 are applied in the experiments and the heat release rate (HRR) is measured.

3. RESULTS AND DISCUSSION

3.1 Kinetic properties estimation for wood

Figure 1 shows an example of mass loss rate curves for wood at three different heating rates: 5, 20 and 60 K/min. The uncertainty of three repeating tests is within 5%, showing an excellent repeatability. All the curves have a shoulder region, a noticeable peak and a long tail region, which indicates the existence of multiple reactions. Therefore, one widely used three-

component scheme (hemicellulose, cellulose and lignin) [1], is firstly adopted to analyse the decomposition process of wood.

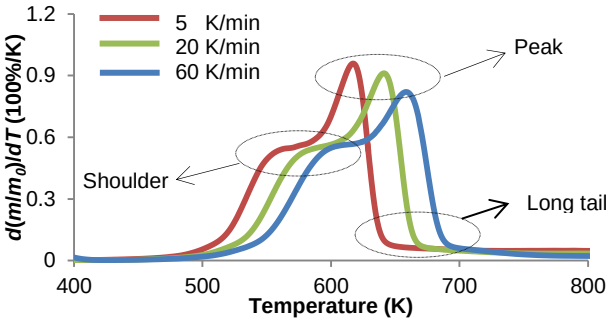

Figure 1 Mass loss rate curves at 5, 20 and 60 K/min

As proposed by Kissinger [2], the reaction rate ($d(m/m_0)/dT$) reaches a maximum value when $d(m/m_0)^2/dT^2$ equals zero. Therefore, the curves $d(m/m_0)^2/dT^2$ are plotted to identify $T_{i,p}$ for the maximum reaction rate of each reaction. Figure 2a illustrates the curves $d(m/m_0)/dT$ and $d(m/m_0)^2/dT^2$ at a heating rate of 5 K/min as an example to locate the $T_{i,p}$ values for each component. When the three-component scheme is applied, the curve $d(m/m_0)^2/dT^2$ is zero at temperatures of 618 K and 665 K, which correspond to the maximum reaction rate of hemicellulose and lignin component respectively. However, there is not a clear zero value on the $d(m/m_0)^2/dT^2$ curve for the hemicellulose region, which is possibly affected by nearby hidden reactions. Thus, a temperature of 572 K for a local minimum value in the hemicellulose region is considered to represent the T_p. In order to further interpret the possible reactions, two components, hemicellulose 1 and hemicellulose 2, are proposed to describe the reaction at the hemicellulose region instead of one component. Hence, a four-component scheme is depicted in Figure 2b, with two assumed components for the hemicellulose reaction regions at $T_{i,p}$ of 550 K and 576 K respectively, while the reactions for cellulose and lignin are the same as the three-component scheme. Table 1 summarises the $T_{i,p}$ values for each reaction at heating rates of 5, 20 and 60 K/min based on the proposed multiple-component schemes.

According to Table 1, the linear relationship of $ln\ (\beta/T_{i,p}^2)$ and $1/T_{i,p}$ for each component is plotted in Figure 3a and Figure 3b. Therefore, the E_i and A_i of each component can be calculated from the slope and intercept of each line based on Equation 3. The mass fraction (f_i) value of each component is determined by comparison of experimental results and the results calculated from Equation 2.

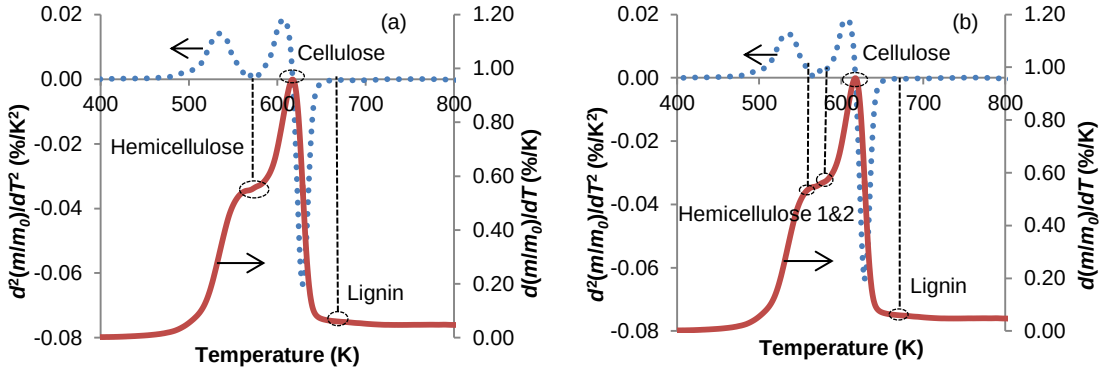

Figure 2 Decomposition curvatures: (a) three-component; (b) four-component.

Table 1 Summary of $T_{i,p}$ for three-component and four-component schemes

β (K/min)	Three-component	Four-component		Three-component & four-component	
	Hemicellulose	Hemicellulose 1	Hemicellulose 2	Cellulose	Lignin
5	572 K	550 K	576 K	618 K	650 K
20	595 K	575 K	600 K	641 K	685 K
60	615 K	595 K	623 K	659 K	706 K

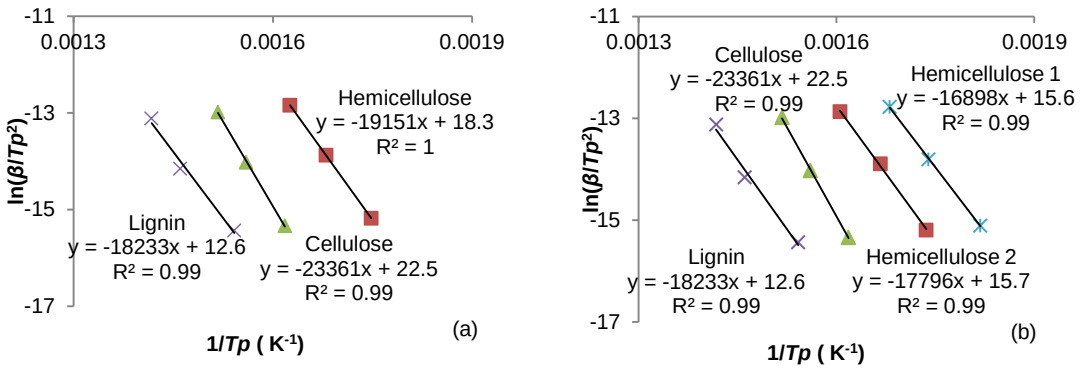

Figure 3 $ln(\beta/T_p^2)$ v.s. $1/T_p$: (a) three-component; (b) four-component.

Table 2 lists the results of kinetic properties and mass fraction for each component based on the analytical method for the three-component scheme and four-component scheme. In addition, the GA searching method is applied to inversely search the kinetic parameters of E, A and n for the three-component scheme. The three sets of TG data under different heating rates of 5, 20 and 60 K/min are chosen for the optimisation. The best solutions are listed in Table 2.

Table 2 Results of kinetic triplet and mass fraction (f_i) for each component

Methods	Components	E_i (J/mol)	A_i (s^{-1})	n_i	f_i
Analytical method	Hemicellulose 1	1.40×10^{5}	$1.01E\times10^{11}$	1	0.15
four-component	Hemicellulose 2	1.48×10^{5}	1.20×10^{11}	1	0.17
scheme	cellulose	1.94×10^{5}	1.30×10^{14}	1	0.45
	Lignin	1.52×10^{5}	5.57×10^{9}	1	0.13
Analytical method	Hemicellulose	1.59×10^{5}	1.70×10^{12}	1	0.32
three-component	cellulose	1.94×10^{5}	1.30×10^{14}	1	0.45
scheme	Lignin	1.52×10^{5}	5.56×10^{9}	1	0.13
GA	Hemicellulose	1.41×10^{5}	1.54×10^{11}	1.54	0.38
three-component	cellulose	1.87×10^{5}	3.36×10^{13}	0.94	0.40
scheme	Lignin	1.19×10^{5}	2.14×10^{10}	4.41	0.12

Note: 10% mass fraction is assumed for the moisture content.

3.2 Simulation results of TG experiments

Based on the TG experiments, FDS6 simulations are conducted in the absence of gas phase computations to represent the decomposition process within a nitrogen environment. The gas temperature is set to ramp up linearly at 5, 20 and 60 K/min. In the simulations, each component is assumed to undergo a single step reaction to generate gas and solid products. The outputs are recorded in the form of a normalised mass loss rate for comparison with the TG experimental data.

Figure 4 illustrates the comparison of the experimental result and the FDS6 simulation results using the properties derived from the different methods at 5 K/min heating rates. Curves 4C_KA and 3C_KA denote the FDS6 simulations that adopt the kinetic properties derived from the Kissinger analytical method for the four-component and three-component schemes respectively. Curve 3C_GA indicates where the properties used in the FDS6 simulations are those obtained from the GA analysis for the three-component scheme.

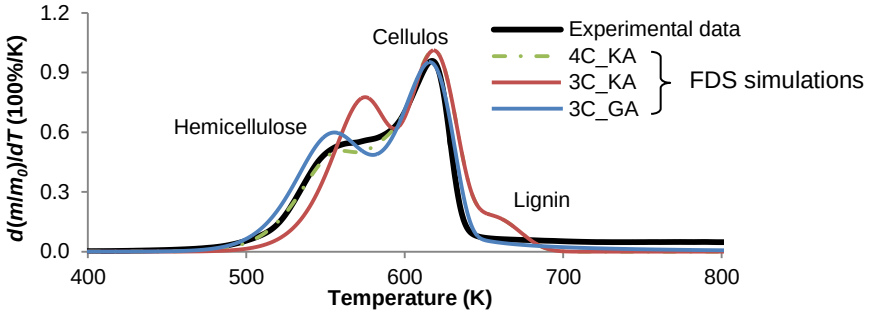

Figure 4 Comparison for TG simulation and experimental results at 5 K/min

Generally, all of the proposed schemes can effectively predict the main features of the decomposition curve of wood. The differences in the FDS6 simulation curves are mainly at the hemicellulose and the lignin reaction regions. Mathematically, the shape of reaction curves is determined by the kinetic triplets. If the values of E and A are fixed, the sharpness of the curve for a reaction is controlled by the reaction order [1, 6] and the magnitude of the peak for the reaction can be changed by the mass fraction of each component. Even though the sharpness of the curve for a reaction is fixed by the first reaction order, the adjustment in the mass fraction of each component can still effectively change the peak value of the reaction to fit the experimental curve. In the application of the Kissinger analytical method (where n=1), it is found that when two components with two small mass fractions are used to describe a reaction, the decomposition curve becomes flatter than the curve based upon one component with a large mass fraction. As shown in Figure 4, the simulation based on the four-component scheme presents the hemicellulose reaction features better than the results from the traditional three-component scheme in the case of using the first reaction model. However, when a free reaction order is applied from GA, the sharpness of the reaction curve can be shaped freely with less effect from the defined mass fraction of the component. For instance, the simulation result for lignin, with a reaction order of 4.41, gives a better fit to the experimental result. Figures 5a and 5b compare the heating rate at 20 K/min and 60 K/min; they demonstrate the same features as shown in Figure 4.

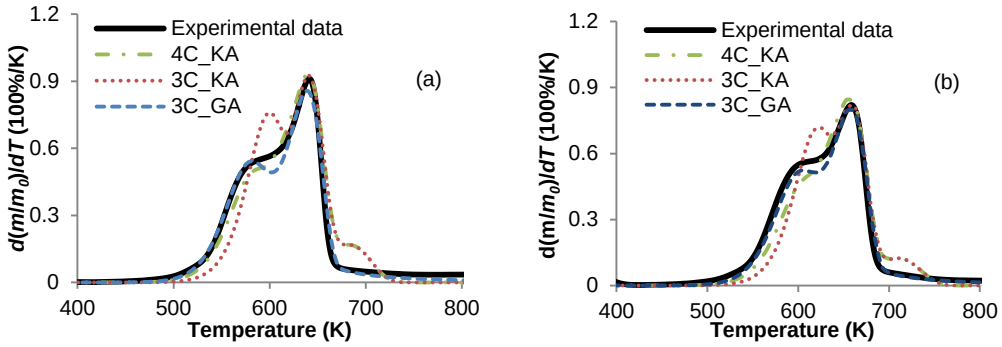

Figure 5 Comparison for TG simulation and experimental results: (a) 20 K/min; (b) 60 K/min.

3.3 Simulation results of cone calorimeter experiments

Two sets of cone calorimeter FDS6 simulations are carried out with external heat fluxes of 35 and 50 kW/m^2. In each simulation, a domain with dimensions of 220 mm × 220 mm × 1200 mm is used to ensure the fire plume can be fully captured and the loss of heat to the outside of domain can be effectively minimised. A simulated 100 mm × 100 mm × 21.5 mm thick sample is placed at the centre of both the X and Y axes, and 250 mm above the bottom of the domain. In order to compute the reactions and heat transfer in the solid sample, the size of mesh cells for the solid phase is automatically defined to be smaller than the square root of the diffusivity of the samples in FDS6 [3], which is different from the cell size set-up in the gas phase. A 10 mm cell is applied to the gas phase computations which gives results comparable to those produced using a cell size of 5 mm but within a reasonable computational time. The incident heat fluxes from the cone heater used in the experiments are simplified by adding an external heat flux to the surface of the sample rather than simulating the cone heater above the sample. As a result of the aim of this study, the only variations in the simulations are the kinetic parameters. Other parameters are kept fixed in all of the simulations as listed in Table 3.

Table 3 Parameters defined in FDS cone calorimeter simulations

Item	Wood	Char
Thermal conductivity (W/mK)	-0.62 + 0.0038T - 4×10^{-6}T^2 [7]	4.43×10^{-2} + 1.48×10^{-4}T [7]
Specific heat (J/kg/K)	3.87T + 101.3 [8]	714 + 2.3T - 8×10^{-4}T^2 - 3.7×10^{-7}T^3 [8]
Heat of combustion (MJ/kg)	12.1 MJ/kg **	-
Density (kg/m^3)	566 kg/m^3 **	150 kg/m^3, based on [9]

** The lab results are provided by the Land Transport Authority (LTA) of Singapore.

The FDS6 simulation results at incident heat fluxes of 35 and 50 kW/m^2 are shown in Figure 6a and Figure 6b. Comparison shows that there is no significant difference in the HRR predictions by applying different kinetic properties derived from the different component schemes, and there is no obvious advantage in the simulation results with using the GA searched parameters.

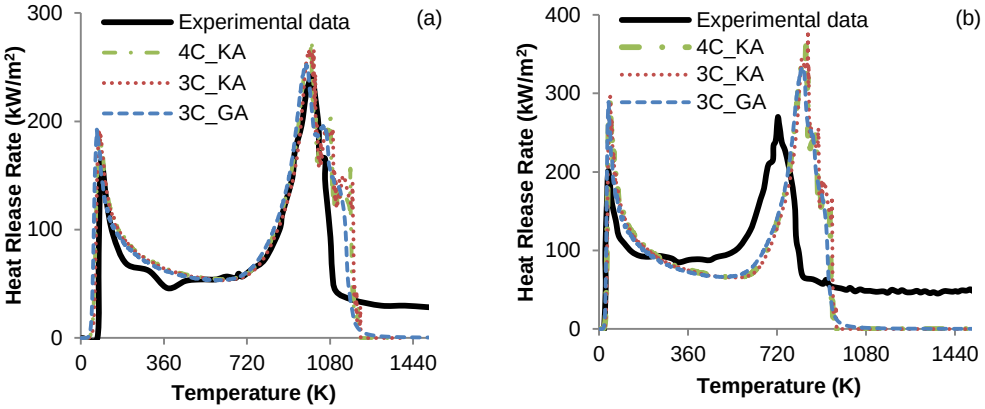

Figure 6 Cone calorimeter simulations and experimental results: (a) 35 kW/m^2; (b) 50 kW/m^2

The similarities in the simulation results obtained by using different model derived kinetic properties suggest that the kinetic properties of wood are not material dependent parameters, which agrees with Matala's [6] interpretation. These parameters are not unique and they can be defined in different ways based on the models or assumptions applied. In terms of the accuracy of the predictions for HRR in FDS6, all the simulations effectively demonstrate the features of the HRR curve for wood obtained from cone calorimeter experiments with the first peak in HRR after ignition and the second peak after a long period of energy dissipation. The FDS6 result for the 35 kW/m^2 heat flux is a close fit to the experimental curve, while the FDS6 result for 50 kW/m^2 gives higher values for the peak HRR and a longer energy dissipation time compared to the results shown in the experimental curve. The simulation results do not show the final char oxidation process. These differences in the burning behaviour of wood between the simulation results and experimental results are due to the HRR predictions in FDS6 are not solely determined by the kinetic properties but also rely on the choice of other parameters, the sensitivity of which needs further analysis.

5. CONCLUSIONS

This study applies the different component schemes to predict the pyrolysis and burning behaviour of wood in FDS6. In the simulations of the TG experiments, the pyrolysis behaviour

for the hemicellulose reaction can be more effectively described by two components than one in the case of using the first reaction order model. The parameters determined by the analytical method using the four-component scheme and the GA method give similar results. However, the use of four-component scheme may increase the complexity of simulations and it is difficult to justify the two reactions for the hemicellulose of wood. On the other hand, the free use of the reaction order allows the GA parameters to properly present the lignin reaction. There is no significant difference in the predictions of HRR in the cone calorimeter simulations when applying the different kinetic properties and the different component schemes. For future work it is worth investigating whether the application of the GA method to determine the kinetic properties of wood can result in a simpler component scheme for the predictions of burning behaviour of wood.

6. AKNOWLEDGMENTS

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